Preparation of *c*-Axis Oriented La₂CuO₄ Thin Films on the Si Substrate by Pulsed Laser Deposition

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The parent materials of the first high-T_C cuprate, La₂CuO₄ (LCO) are known to be correlated with Mott insulators that become metallic and superconducting upon doping with charge carriers.[1] A large number of researches have been performed on bulk samples in the LCO-based materials due to their simple chemical composition and crystal structures as well as the rich physical properties.[2] The transition from the Mott-Hubbard insulating state to the metallic state is called the metal insulator transition (MIT),[3] and is a topic of great current interest. As an important application of the MIT, a high-speed Mott switching device using an abrupt current jump was predicted for a transistor.[4]

LCO is known to have three different structures,[5] T-phase (K₂NiF₄-type) containing edge-shared CuO₆ octahedra arranged in a planar array, T'-phase (Nd₂CuO₄-type) in which the apical oxygen in the T-phase is shifted away from the Cu atoms, and S-phase (Sr₂CuO₃) which has isolated CuO₃ chains running along the *a*-axis of the orthorhombic structure. Transitions among T, T' and S phases were found in the annealing process of bulk LCO. These are quasi-two-dimensional materials which consist of layers of copper-oxide planes separated. It seems that most of the properties are determined by electrons moving within CuO₂ planes.

The preparation of the thin film[6] is a key point to develop the devices such as thermal switching, thermochromatic coatings, non-volatile memory *etc*. applying MIT properties of LCO. High quality thin film of LCO is required for a variety of fundamental studies. The electrical and transport properties of LCO-based thin films are highly sensitive to the degree of *c*-axis orientation in the film growth and induced strain due to lattice mismatch with the substrate. A large number of substrates have been used to obtain highly oriented LCO thin films with good electrical properties such as NdGaO₃, LaAlO₃, SrTiO₃, and SrLaAlO₃ substrates with a small lattice mismatch.[7] However, these cannot be used in the development of the MIT devices as common substrates because it is too difficult and expensive for the preparation of their single crystalline structure. LCO thin film is required to be grown with *c*-axis orientation on the surface of common substrates such as SiO₂ acting as a gate oxide for fabrication of MIT devices.

In the present work, we report the first preparation of *c*-axis oriented LCO thin films on Si substrate, which is largely lattice-mismatched with LCO, by pulsed laser deposition (PLD) following *in-situ* post-annealing in oxygen ambient. PLD technique is a well-known deposition technique providing stoichiometric transfer of target materials *via* congruent evaporation for a wide range of materials including metals, alloys and oxide films.

Experimental Section

The polycrystalline LCO target was prepared by a conventional solid-state reaction. Stoichiometric amounts of La₂O₃ (99.9%, preheated at 900°C for 12 h) and CuO (99.9%) were thoroughly mixed and heated at 1050°C for 24 hrs in the air. The powder was ground and pressed into pellets under a pressure of about 50 MPa and sintered at 1000°C for 24 h. The ultimate pellet was identified as a single phase of LCO by X-ray diffraction patterns with Cu-K$_\alpha$. LCO thin films were deposited on Si substrate with a typical size of 20×20 mm at various temperature using a frequency tripled Nd:YAG Laser (Quantel, Brilliant II) with 5-ns of pulse width. The laser pulses of 10 Hz were focused onto the rotating target using a quartz lens with 35 cm focal length at a 45° oblique incidence, and the energy density was approximately 2 J/cm². A substrate was set at a distance of 70 mm parallel from the target surface. The grown films were subsequently post-annealed in oxygen ambient at various temperatures. The deposited LCO thin films are reddish and have a typical room-temperature two-point contacting resistance of the order of MΩ, indicating a semiconductor. The structural and phase identification was carried out using an X-ray diffractometer (MacScience Co. MXP-3V) with Cu-K$_\alpha$ radiation. Cross-sectional and plane views were obtained using a scanning electron microscope (SEM) (Hitachi Co. S-4200).
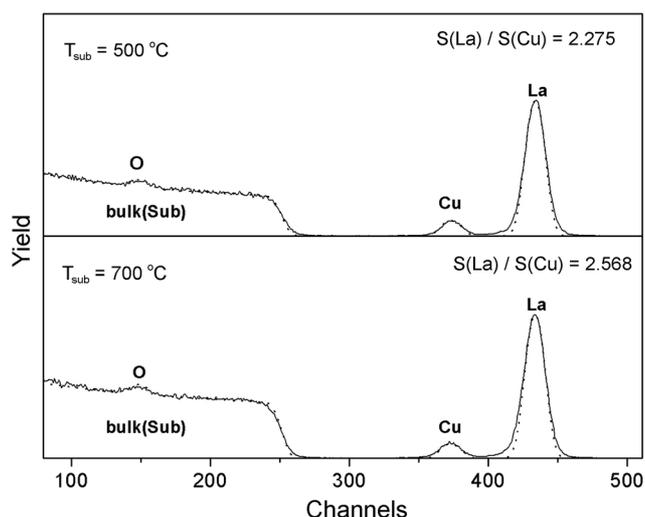
Results and Discussion

Figure 1 shows the XRD spectra of LCO thin films deposited on Si wafer at various growing temperature under oxygen ambient of 26 mTorr for 1 hour. The Si wafers were etched with 5% HF solution for 5 min to remove natural oxide layer before the deposition of LCO. There are three peaks located at about $2\theta = 28.6$, 31.2 and 33.0°, respec-
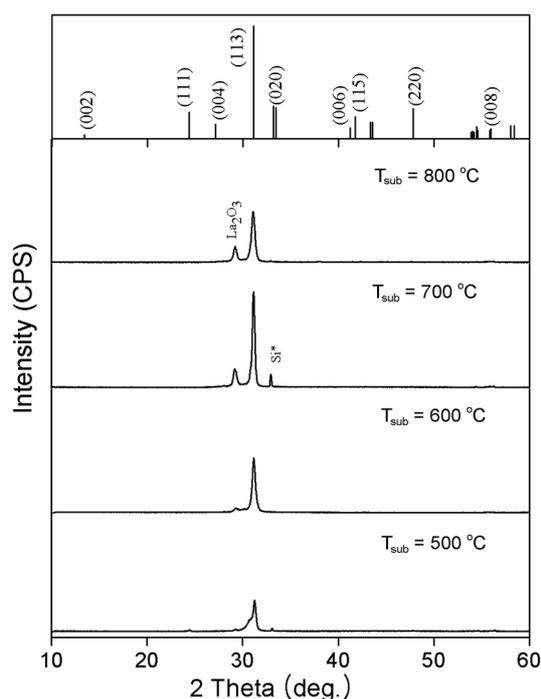
Figure 1. θ-2θ XRD scan of as-deposited La$_2$CuO$_4$ thin films on Si substrate with variation of growing temperature.

Figure 2. Rutherford back scattering (RBS) spectra of as-deposited La$_2$CuO$_4$ thin films on Si substrate.

tively. The most intense peak at about 31.2° corresponds to (113) reflection of LCO, while peak at about 33.0° is identified to forbidden Si (002) diffraction, and is used for calibration of other XRD peaks. XRD spectra show that as-deposited LCO thin films have the predominantly preferential orientation of (113) direction on the Si substrate. It is consistent with the result of Wang *et al.* that the preparation of *c*-axis oriented LCO thin film is difficult since the diffraction-reflection from (00*l*) planes are always accompanied by other reflections such as (113) and (200).[8] As deposition temperature increases, the intensity of (113) peak increases and its width becomes narrower up to 700 °C of deposition temperature. With further increase in the deposition temperature to 800 °C, the intensity of (113) peak decreases somewhat with the broadening of width. The XRD peak at $2\theta = 28.6°$ is not matched with any peak of the LCO phase and corresponds to (101) peak of La$_2$O$_3$ phase. It is interpreted that the secondary phase of La$_2$O$_3$ results in copper deficiency on film formation. In the PLD process, a little difference of composition between thin film and target can be caused by the collisional loss during flight from target to substrate and evaporation of volatile component on the substrate before crystallization. Because of the high vapor pressure of Cu, Cu ablated from the target surface by laser pulse can easily evaporate on the substrate with a high temperature before the formation of the LCO phase. The relative ratio of (101) peak of La$_2$O$_3$ to (113) peak of LCO increases as the deposition temperature increases. The RBS spectra of Figure 2 show that the relative ratio of La to Cu signal of the thin film deposited at 700 °C is higher than that of the thin film deposited at 500 °C although the signals are

not calibrated to an absolute amount. This indicates the Cu deficiency according to evaporation of Cu at the deposition temperature of 700 °C, and is consistent with the formation of secondary phase of La$_2$O$_3$ in XRD results. The appearance of a secondary phase like La$_2$O$_3$ was reported by Tsukada *et al.*[9] when La$_2$CuO$_4$ was exposed to a decreased oxygen partial pressure atmosphere. Since the removal of oxygen destabilizes the crystal structure, reduction leads to defects and these defects cannot be reversed by oxygen annealing due to the evaporation of copper at a high temperature.

Compared with the highly oriented thin films, polycrystalline films can be easily obtained because the LCO films often fabricated were usually found to have other reflections, (113), (200) *etc.* These films are expected to have different behaviors as compared with *c*-axis oriented films regarding the presence of non-*c*-axis oriented crystalinities.[10] The postannealing step is usually carried out to improve the properties of as-deposited thin films such as crystallinity, grain size and stoichiometry of the light component, *etc.* in the thin film processes. To prevent the evaporation of copper, resulting in the formation of a secondary phase of La$_2$O$_3$ in LCO film, as-grown thin films were heated in the chamber under oxygen ambient. Figure 3 shows the X-ray θ-2θ diffraction patterns for the post-annealed LCO thin films at various temperatures under oxygen ambient of 1 Torr for 1 hr after grown at 500 °C. The post-annealed thin film at 500 °C of substrate temperature has two broad humps centered at about 26.3° and 30.0° in an XRD diffraction pattern, which represents that the degree of crystallization is poor because of the low temperature of the substrate. According to Chou *et al.*,[11] these two humps correspond to (011) and (103) peaks of *S*-phase of LCO which has CuO$_3$ chains running along the *a*-axis of the orthorhombic structure, and the intensities of these two humps decrease as the temperature of post-annealing increases. However, the diffraction peaks of (00*l*) with *l* = 2*n* of *T*-phase of LCO, which represent the
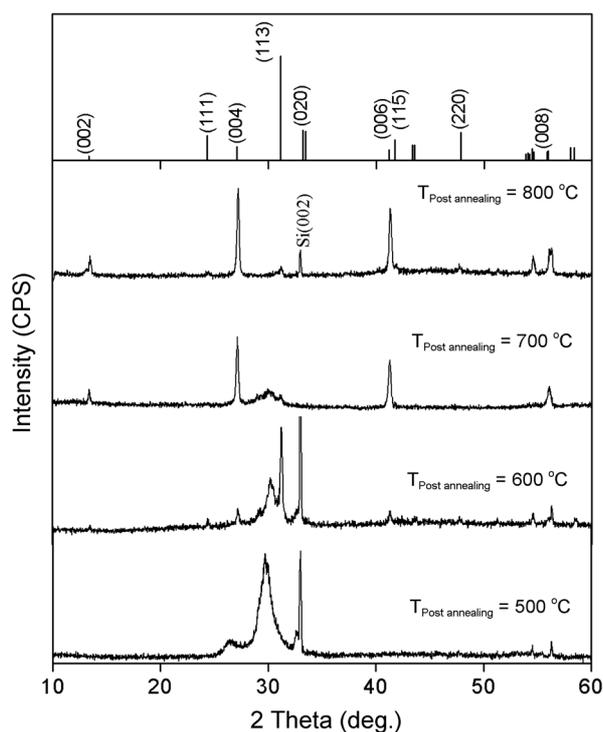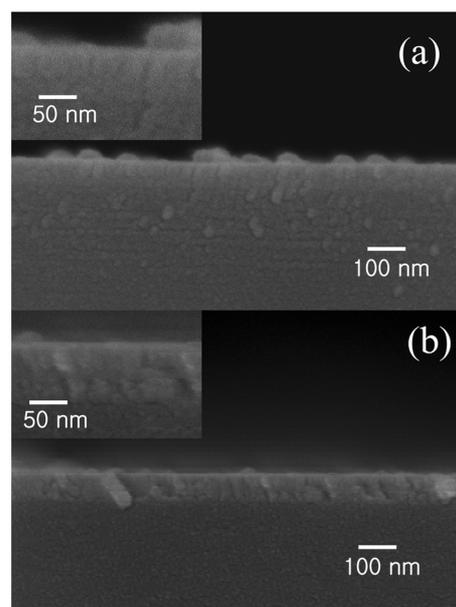
Figure 3. θ-2θ XRD scan of post-annealed La$_2$CuO$_4$ thin films after grown at 500°C on Si substrate.

Figure 4. SEM images of cross section of post-annealed La$_2$CuO$_4$ thin films at 500°C (a) and 700°C (b).

c-axis orientation of thin film, appear to accompany with (113) diffraction from the XRD pattern of the thin film post-annealed at 600°C and are solely present except the diffraction of Si (002) in the XRD pattern of the thin film post-annealed at 800°C. The sole presence of (00*l*) diffractions in the patterns suggests that the film consists of entirely *c*-axis-oriented grains. Performing a least squares refinement on each of these diffractions yields a value of 13.12 Å for the lattice parameter. This is an excellent agreement with the literature value of 13.149 Å, obtained from a bulk prepared sample.

The structural change of LCO thin film of variation with temperature during post-annealing is quite interesting. While many studies have been reported for the film structure according to the variation of substrate[12] and doping content[13] in LCO, it is hard to find a study for the effect of the post-annealing process in formation of the LCO thin film. Comparing with the bulk system of LCO, Chou *et al.*[11] reported the *S*-phase of the oxygen-deficient structure of LCO has the structural phase transition to *T*-phase in the temperature range of 650°C-925°C by heating in an oxygen flow. This supports the XRD spectra which show the mixed phase in post-annealed thin films at 600°C and *T*-phase in that post-annealed above 700°C.

Figure 4(a) and (b) present the cross section images of LCO thin films post-annealed at 500°C and 700°C after grown on Si substrate at 500°C, respectively. The thicknesses of deposited thin films are about 90 nm and the deposition rate is estimated to 0.24 Å/sec in this PLD system. As shown in Figure 4, the boundary between the

thin film post-annealed at 500°C and Si substrate is so blurred that it cannot be definitely found. However, the thin film post-annealed at 700°C shows the discrete boundary with Si substrate. It is well consistent with the degree of crystallization of the thin films as depicted in Figure 3 of XRD spectra of LCO thin films.

It is well known that the epitaxial thin film of LCO with *c*-axis is difficult to grow on Si substrate because its lattice mismatch is too large for LCO. Therefore, it has been reported that the substrates such as LaAlO$_3$, SrTiO$_3$, and SrLaAlO$_3$ with a small lattice mismatch have to be used to grow the *c*-axis oriented thin film of LCO. Especially, to grow that on Si substrate, an interest has developed in the use of buffer layer with a thickness of a few nm's on silicon to maintain an epitaxial relationship. Zirconia stabilized with yttria is at present the most widely used epitaxial buffer layer for Si substrate to grow the thin film of cuprate.[14]

In this study, the preparation of *c*-axis oriented thin film on Si substrate without any buffer layer is quite interesting. The post-annealing is certain to play a decisive part for the structural reorganization of LCO thin film after growing. There are two considerations to explain the formation of oriented thin film. The first consideration is the kinetic aspect of the film orientation to be determined in initial deposition of the thin film. In the beginning of the deposition step, the structure of the first layer should reflect the atomic array of substrate surface and it regressively affects the upper layer in further growth of the thin film. Though the initial orientation is not preferred thermodynamically, its growing proceeds until the strain due to lattice mismatch can be tolerated. If the intrinsic strain incurred during the growth is not so severe, the thin film grows epitaxially on the substrate, and if not, the stress interrupts the epitaxial growth of thin film, resulting in polycrystalline structure with the random orientation.

The second consideration is the thermodynamic aspect. This involves transformation to a more stable structure with lower Gibbs free energy if overcoming the energy barrier for structural change. The energy barrier depends on the degree of crystallization of the thin film. The higher the degree of crystallization of thin film, the more energy is required for transformation of the thin film structure. Though no thermochemical data is available for the stabilization energy to crystal arrangement of LCO thin film, it might be interpreted that (00l) orientation is thermodynamically stable. As a result, the deposited thin film at 500°C which depicts low crystallization in XRD spectrum is suggested to lead the high c-axis orientation by self-organization. It is also understood that the phase transition is interrupted by high activation energy for a structural change, and by irreversible deficiency of Cu for the highly crystallized thin film deposited at a higher temperature. The formation of LCO thin film with a thermodynamically controlled structure seems to be not greatly affected by substrate type. This suggests the capability of preparation of c-axis oriented LCO thin films on the common oxide substrate such as SiO_2 and Al_2O_3 to fabricate the Mott transition field effect transistor (MTFET) devices, and further studies are required to investigate the mechanism on the structural change of the thin film and the effects on the oriented film formation according to the variation of the substrate.

In summary, c-axis oriented thin films of LCO have been successfully prepared on Si substrate, which is largely mismatched with LCO, by pulsed laser deposition. While as-deposited thin films have the predominantly preferential orientation of (113) direction with a secondary phase of La_2O_3, the sole c-axis orientation with (00l) direction is shown in the post annealed thin film at 700°C after being grown at 500°C. It is interpreted that the aligned structure of CuO_2 layer is thermodynamically more stable and shows the capability of preparation of c-axis oriented LCO thin films on the common oxide substrate such as SiO_2 and Al_2O_3 to fabricate the MTFET devices

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